Chapter 12

Basic Cement Chemistry

BASIC CEMENT CHEMISTRY CHEMICAL COMPOSITION

Elemental composition in weight percentage. By convention, the elements are expressed in form of their oxides (exception: Cl, F).

Table 1 **Usual sequence of elements in cement analysis:**

	Examples	
	Limestone	**Clinker**
L.o.I.[1]	42.2	0.24
SiO_2	1.9	22.7
Al_2O_3	0.81	5.7
Fe_2O_3	0.52	1.9
CaO	52.2	66.0
MgO	1.4	2.0
SO_3	0.56	0.33
K_2O	0.22	0.74
Na_2O	0.08	0.09
TiO_2	0.05	0.18
$Cr2O_3$		
$Mn2O_3$	0.02	0.03
P_2O_5	0.01	0.05
Cl	0.01	0.01
F		

[1)] loss on ignition, e.g. at 1050°C
mainly due to H_2O, CO_2

1. CHEMICAL FORMULAE

The chemical formula indicates the elements occurring in a chemical compound:

- for a molecular compound, type and absolute number of elements in a molecule are given

H_2O	O_2	C_6H_6
water	oxygen	benzene

- for a mineralogical compound, type and relative number of elements are given

SiO_2	CaO	$CaCO_3$	Ca_3SiO_5
quartz	lime	calcite	alite

Note: In mineralogical compounds, the elements need not necessarily occur in simple numerical ratios (impurities, solid solution)

- in the cement chemistry, shorthand's are often used:

CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	H_2O
C	S	A	F	$\bar{S}$	H

Examples:
C_3S for Ca_3SiO_5 (alite)
C_2S for Ca_2SiO_4 (belite)
C_3A for $Ca_3Al_2O_6$ (aluminate)
C_4AF for $Ca_4Al_2Fe_2O_{10}$ (ferrite)

2. MINERALOGICAL COMPOSITION

Table **Composition of a material, expressed in weight-percentage of the occurring minerals**
Example:

	Limestone	
Calcite	$CaCO_3$	90%
Dolomite	$CaMg(CO_3)_2$	5%
Quartz	SiO_2	5%

	Clinker	
Alite	C_3S	58%
Belite	C_2S	23%
Aluminate	C_3A	9%
Ferrite	C_4AF	7%
Periclase	MgO	1%
Arcanite	K_2SO_4	1%
Free lime	CaO	1%

Table **Difference between chemical and mineralogical composition:**

		Limestone		
Mineralogical	comp.		Chemical	comp.
Calcite	$CaCO_3$	90%	L.O.I.(CO_2)	40,0%
Dolomite	$CaMg(CO_3)_2$	5%	SiO_2	5,0%
Quartz	SiO_2	5%	CaO	53,9%
			MgO	1,1%

(simplified, minor elements not included)

3. CHEMICAL PARAMETERS FOR CEMENT-SPECIFIC MATERIALS

3.1 Titration

Content of carbonates as determined by acid-base titration, expressed as $CaCO_3$
% Titration = 1.786 CaO + 2.48 MgO

Applied for:

- Limestone
- Marl
- Raw Meal

3.2 Lime Saturation

$$LS = \frac{CaO \times 100}{2.80\,SiO_2 + 1.18\,Al_2O_3 + 0.65\,Fe_2O_3}$$

or

$$LSF = \frac{CaO}{2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3}$$

The LS is a measure to which extent the CaO-richest compounds C_3S, C_3A and C_4AF can be formed without the necessary presence of free lime. At LS > 100, free lime will unavoidably be present after burning.

Applied for:

- Raw meal
- Clinker
- Cement: neat OPC only
  $CaO = CaO_{total} - 0\ 7\ SO_3$

Usual range in clinker: 85 - 100

Note: The influence of MgO can be accounted for

$$LS = \frac{(CaO + 0.75\,MgO) \times 100}{2.80\,SiO_2 + 1.18\,Al_2O_3 + 0.65\,Fe_2O_3}$$

max. 2 % MgO may be introduced in formula (not applied in cement specifications)

3.3 Silica Ratio

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}$$

Applied for

- Siliceous-argillaceous raw components
- Raw meal
- Clinker
- Cement

2
Usual range in clinker: 1.8 - 3.6 - 2,4 liquide

3.4 Alumina Ratio

$$AR = \frac{Al_2O_3}{Fe_2O_3}$$

Applied for

- Siliceous-argillaceous raw components
- Raw meal
- Clinker
- Cement

liquide ↑
Usual range in clinker: 1 - 3 → visqueux
↓ liquide
idéal 1.5 ; 1.3

3.5 Na_2O-equivalent

Total alkali content, expressed as Na_2O
Na_2O-equivalent = $Na_2O + 0.658\ K_2O$

Note: Limit for low alkali cement

Na_2O-equiv. $\leq$ 0.6 %

Applied for Clinker

Cement

4. CONTENT OF CLINKER MINERALS ACCORDING TO BOGUE

Percentage content of clinker minerals, assuming that chemical equilibrium is attaint, and that no impurities are present
$C_3S = 4.07CaO - 7.6SiO_2 - 6.73Al_2O_3 - 1.43Fe_2O_3$

$C_2S = 8.6SiO_2 + 5.07Al_2O_3 + 1.08Fe_2O_3 - 3.07CaO$
or $2.87SiO_2 - 0.754C_3S$

$C_3A = 2.65Al_2O_3 - 1.69Fe_2O_3$

$C_4AF = 3.04Fe_2O_3$

In reality, the mineralogical composition of industrial clinkers differs to some extent from that calculated according to Bogue.

4.1 Applied for

- Cement:
  - OPC only (excl. blended cements)
  - correction for CaO in $CaSO_4$:
    $CaO = Ca_{tot} - 0\ 70\ SO_3$
  - For ASTM: TiO_2 and P_2O_5 to be added to Al_2O_3
- Clinker:
  - CaO can be corrected for "$CaSO_4$" or for free lime, depending on objective of calculation

5. SIGNIFICANCE OF CLINKER MINERALS FOR CEMENT PROPERTIES

C_3S Contributes to early and late strength (1 d - ...)
Increases heat of hydration

C_2S Contributes to late strength (28 d - ...)

C_3A Contributes to early strength (1 - 3 d)
Increases heat of hydration
Impairs resistance to sulphate attack

C_4AF Little effect (broyage)

6. SIGNIFICANCE OF CLINKER MINERALS FOR ASTM CEMENT TYPES

Type I	Portland no restrictions regarding clinker minerals
Type II	Portland with moderate sulphate resistance C_3A max. 8 %
Type III	Portland with high early strength C_3A max. 15 %
Type IV	Portland with low heat of hydration C_3S max. 35 % C_2S min 40% C_3A max. 7 %
Type V	Portland with high sulphate resistance C_3A max. 5.0 % $C_4AF + 2\ C_3A$ max. 25 % or $C_4AF + C_2F$ max. 25 %

7. RELATIONSHIPS BETWEEN CHEMICAL MODULI AND CLINKER MINERALS

The following relationships are calculated for simplified clinker compositions, i.e. only containing the main elements SiO_2, Al_2O_3, Fe_2O_3, CaO

Fig: **Clinker Minerals as Function of LS**
SR=2.5 AR=1.5

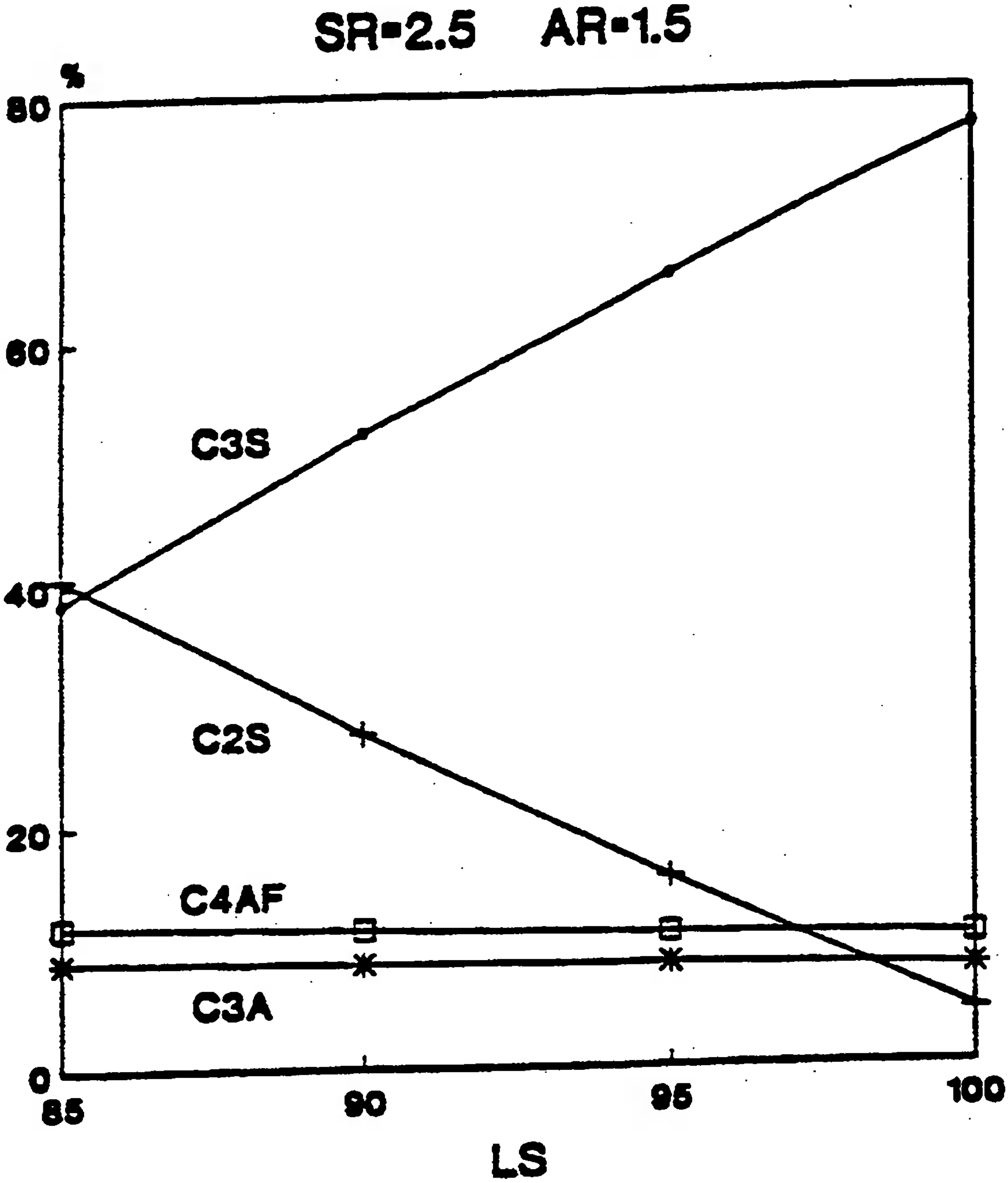


Fig: **Clinker Minerals as Function of SR**
LS=95 AR=1.5

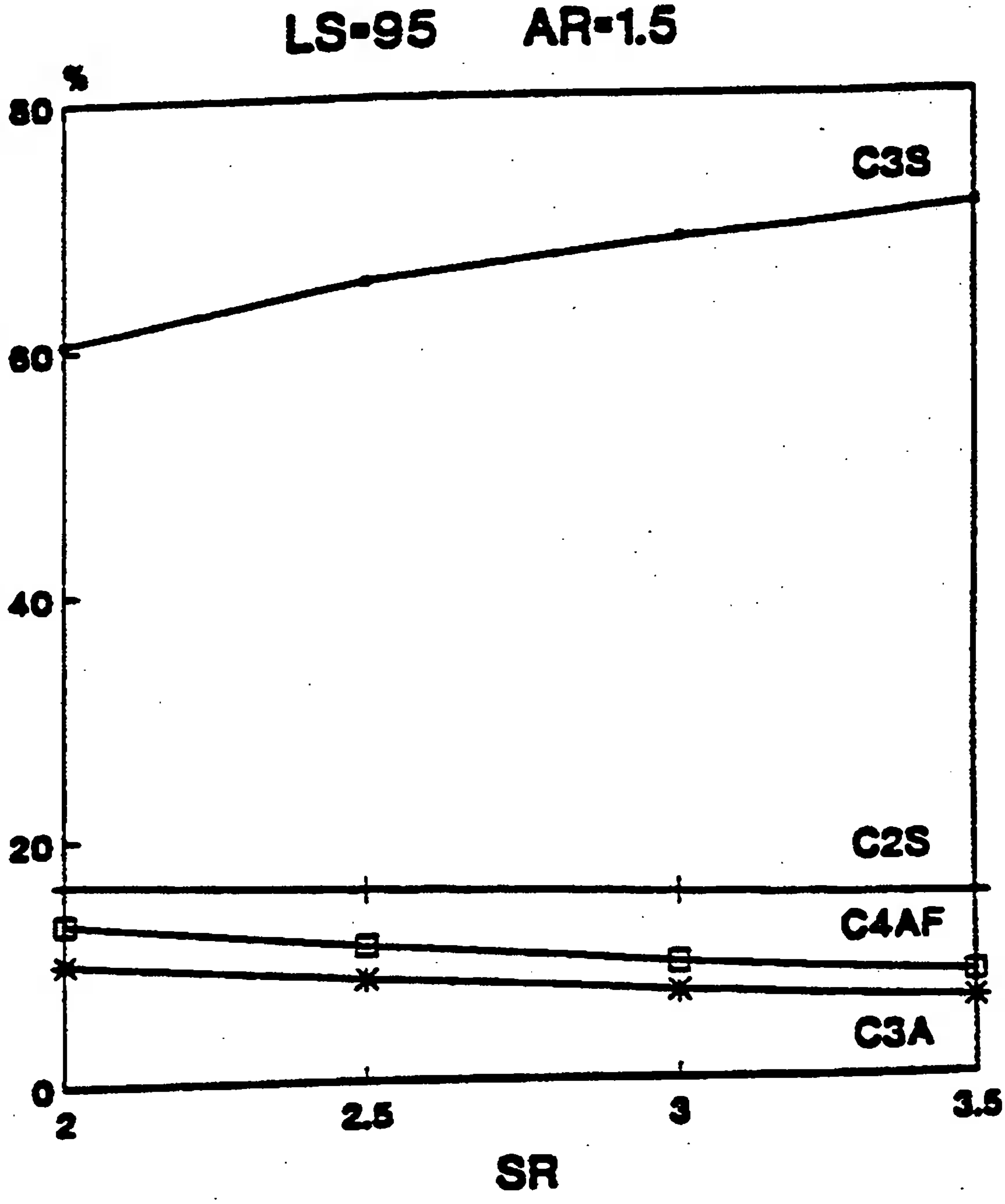
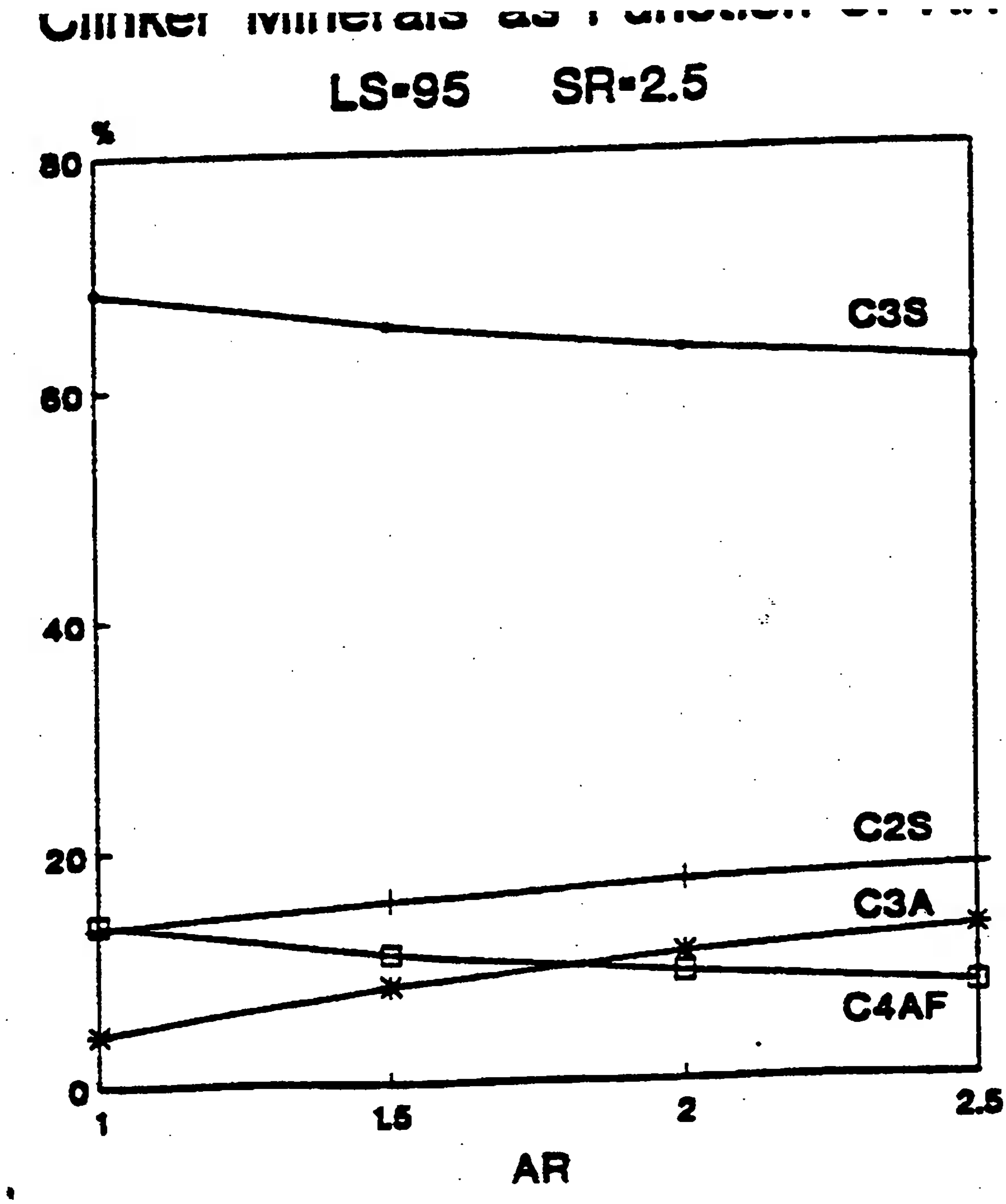


Fig: Clinker Minerals as Function of AR
LS=95 SR=2.5



8. EXERCISE FOR CALCULATION

	Raw Mix	Potential clinker composition
L.o.I.	35.1	....
SiO_2	14.3	22
Al_2O_3	3.6	5,55
Fe_2O_3	2.0	3,08
CaO	42.0	64,7
MgO	1.8	2,77
SO_3	0.25	0.38
K_2O	0.63	0,97
Na_2O	0.22	0,34
TiO_2	0.17	0,26
Mn_2O_3	0.10	0,15
P_2O_5	0.06	0,09
Cl	0.01	0,0

Titration	....	
LS	97,12	99,22
SR	....	....
AR	....	....

Na_2O-equiv.	....
C_3S	56,4
C_2S	....
C_3A	....
C_4AF	....

$$\text{Ck factor} = \frac{100}{100 - \text{LoI}}$$

Ck = 1,54

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Loss on Ignition	
SiO_2	22.03
Al_2O_3	5.55
Fe_2O_3	3.08
CaO	64.71
MgO	2.77
SO_3	0.39
K_2O	0.96
Na_2O	0.34
TiO_2	0.26
Mn_2O_3	0.15
P_2O_5	0.09
Cl	0.02
F	
TOTAL	100.35
Freelime	
Insoluble Residue	

LS	92.13
SR	2.55
AR	1.80
C_3S	54.3
C_2S	22.2
C_3A	9.5
C_4AF	9.4
C_3S	54.3
C_2S	22.2
C_3A	9.5
C_4AF	9.4
Titration	-
Clinkerfactor	-
Na_2O-eq.	0.97
Mol. Alk./SO_3	3.16

cem-calc.xls

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Loss on ignition	35.1
SiO_2	14.3
Al_2O_3	3.6
Fe_2O_3	2.0
CaO	42.0
MgO	1.8
SO_3	0.25
K_2O	0.62
Na_2O	0.22
TiO_2	0.17
Mn_2O_3	0.10
P_2O_5	0.06
Cl	0.01
F	
TOTAL	100.23
Freelime	
Insoluble Residue	

LS	92.13
SR	2.55
AR	1.80
C_3S	54.3
C_2S	22.2
C_3A	9.5
C_4AF	9.4
C_3S	
C_2S	
C_3A	
C_4AF	
Titration	79.48
Clinkerfactor	1.54
Na_2O-eq.	0.97
Mol. Alk./SO_3	3.20